Modification of Kinetic models for the description of thermal dissociation processes in polydisperse system.

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Abstract: - Relationships have been established between the average transformation degree and the dissociation time for polydisperse granular material, taking into account its grain size distribution. It has been checked in which cases the kinetic curves, obtained by a numerical solution, can be described in terms of the chosen F1, F0,D1 equations (models).

Key-Words: - kinetics, kinetic models, thermal dissociation of solids, polydisperse system.

1 Introduction

The description of thermal dissociation of solids by means of the well-known kinetic equations, is usually based on the single grain model.

If the reaction system contains X grains of identical initial size, then the kinetic equation should not change, because the transformation degree for X equal grains is calculated analogously to that for a single grain.

In the case of polydisperse systems (with different grain size) the transformation degree is different for grains with different initial dimensions and it can be described by the following relation:

$$\overline{\alpha} = 1 - \int_{R_i=0}^{R=R_m} [1 - \alpha(R_i)] f(R) dR$$
(1)

where: $\overline{\alpha}$ - mean value of transformation

degree; $\alpha(R_i) \in \langle 0; 1 \rangle; \alpha(R_i)$ - transformation degree for grain fraction of initial radius R_i , $f(R_i)$ - density function for grain size distribution characteristic for the given polydisperse system; (R_m) - final radius of the coarsest grains present in the reaction system. The paper's aim was to to test the possibility of using all well-known kinetic equations for the description of thermal dissociation processes occurring in polydisperse system.

As examples I've chosen the following equations, F1:

$$-\ln(1-\alpha)^{1/n} = kt$$
 (2)

F0:
$$\alpha = kt$$
 (3)
rd $D_{1}(1, \alpha) \ln (1, \alpha) + \alpha = kt$ (4)

and D1:(1-
$$\alpha$$
) ln (1- α)+ α =k t (4)

Those equations have been utilized for description of many thermal dissociation reactions. They've been derived with assumptions that the process of thermal dissociation of the type: $A_{(s)} \leftrightarrow B_{(s)} + C_{(g)}$ proceeds by instantaneous formation of nuclei of new phase (reaction product) on the surface of the reacting cylindrical or prism-shaped grain or the nuclei of the new phase are not formed on some crystal faces and the migration of the phase boundary substrate- product (reaction boundary) is considered only for those crystal planes on which the nuclei have been formed.

The exponent reflexes the number of directions in which the phase boundary propagates, Eq.(3) which exponent is equal 1 describes the case of where the phase boundary migrates with a constant rate in one direction.

This equation $\alpha = kt$ describes very well the cases where the reaction surface is constant and it does not shift inside the grain bulk. The possibility of using the equation (3) have been checked for mathematical description of thermal dissociation of polydisperse solids for such systems in which the grain size distribution is described in terms of either normal or Rosin–Rammler-Sperling distribution i.e. where the functions of density of the grain size distribution are given respectively by the following equations:

$$f_{\rm N}(R) = \frac{1}{\delta \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{R-\overline{R}}{\delta}\right)^2 \quad (5)$$
$$f_{\rm R}(R) = n \left(\frac{1}{R}\right)^n R^{n-1} \cdot \exp\left[-\left(\frac{R}{\overline{R}}\right)^n\right] \quad (6)$$

and the distribuants are expressed by the following relationships:

$$F_{\rm N}(R) = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{R_z} \exp[-B(R_z - 1)^2] dR_z (7).$$

$$F_{\mathfrak{R}}(R) = 1 - \exp(-R_{z}^{n}) \qquad (8).$$

In the above equations:

 δ -variance, \overline{R} -mean grain radius,

$$B = \frac{\overline{R}}{2\delta^2}$$
, $\overline{R} = 1$ and $R_z = \frac{R}{\overline{R}}$.

2 Problem Formulation

A dimensionless variable $R_z = \frac{R}{\overline{R}}$ has been introduced to the kinetic equation (3) and maximum

transformation time has been calculated for the fraction of radius R_i it follows that transformation of i-th fraction for α =1 is $t_{m,i}$.

Assuming in Eq.(3) $k=k_i/R_i$ one obtains for a fraction of R_i and $\alpha=1$:

$$t_{m,i} = \frac{R_i}{k_{1,i}} = \frac{R_{z,i} \cdot \bar{R}}{k_{1,i}}$$
(9)

Hence:

$$\theta_{k,i} = \frac{k_{1,i} \cdot t_{m,i}}{\overline{R}} = R_{z,i}$$
(10)

The transformed Eq.(3) and the density function $f_N(R)$ are inserted into Eq.(1) and assumption is made that $dR = \overline{R} \cdot dR_c = \overline{R} \cdot \theta$, hence:

$$\overline{\alpha} = 1 - \left\{ \int_{R=0}^{R=R_m} \left[1 - \alpha(R_1) \right] \cdot \frac{1}{\delta\sqrt{2\pi}} \cdot \exp\left[-\frac{1}{2} \left(\frac{R - \overline{R}}{\delta} \right)^2 \right] dR \right\}$$
(11)

Assuming $\overline{R}=1$ we obtain $\theta_{k,i} = k_i / t_{m,i}$, hence:

$$\alpha(R_i) = \theta \tag{12}$$

and Eq.(3) becomes:

$$\overline{\alpha} = 1 - \left\{ \int_{\theta_i}^{\theta} \left[(1 - \theta) \cdot \frac{1}{\delta \sqrt{2\pi}} \exp\left\{ -\frac{1}{2} \left(\frac{R - 1}{\delta} \right)^2 \right\} \right] d\theta \right\}$$
(13)

Equation (13) comprises the terms $:\frac{1}{\delta\sqrt{2\pi}}$ and

 $\frac{1}{2}\left(\frac{R-1}{\delta}\right)^2$. We can introduce a dimensionless variable

$$B = \frac{1}{2\delta^2}$$
 in the former and assume $\overline{R} = 1$

$$\delta = \sqrt{1/2B}$$
(14)

and for
$$\delta^2$$
 later equation assumes the form:

$$-\frac{1}{2}\frac{(R-1)^2}{\delta^2} = -\frac{1}{2}\left(\frac{(R-1)^2}{\frac{1}{2B}}\right) = -B(\theta-1)^2$$
(15)

After introduction of relationships (14), (15) to Eq. (13) and for $dR = \overline{R} \cdot dR_z = \overline{R} \cdot \theta$, we obtain in the case of Eq.(3) for normal distribution and Rosin–Rammler–Sperling distribution respectively:

$$\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_i}^{\theta_m} \{ (1 - \theta) \cdot \exp[-B(\theta - 1)^2] \} d\theta \right\}$$
(16)

$$\overline{\alpha} = 1 - \left[n \int_{\theta_i}^{\theta_m} (1 - \theta) \cdot \theta^{n-1} \cdot \exp(-\theta^n) d\theta \right]$$
(17)

3 Problem Solution

Equations (16) and (17) have no analytical solution. The following method has been applied for performing numerical calculations in the language Turbo Pascal 6.0:

The calculations were performed for the values of B and θ in the case of normal distribution and for n and θ in the case of Rosin–Rammler–Sperling distribution.

The values of $\overline{\alpha}$ for B $\epsilon < 0.001;1000>$ and for $\theta \epsilon < 0.001;2>$ where calculated from Eq. (16).

After necessary search among B values we have those for which the kinetic curves begin at the origin as in Fig.1.



Fig.1.kinetic curves for normal distribution

The kinetic curves determined have been described in terms of Eq.(16) as a modified Eq.(3) and the results of calculations are given in Fig.2. and Fig.3.



Fig.2.Curves from Eq.(3).-normal distribution.



Fig.3. curves from Eq.(3) with approximation.

In the same way the values of $\overline{\alpha}$ for $n \in <0.001;1000>$ and $\theta \in <0.001;2>$ where calculated from Eq.(16) as a modified Eq.(3), Fig.4.



Fig.4.kinetic curve for Rosin-Rammler-Sperling distribution.

The kinetic curves found were described in terms of Eq.(3). The results of calculations are given in Fig.5 and Fig.6.



Fig.5. Curves from Eq.(3) -Rosin-Rammler-Sperling distribution.



Fig.6. curves from Eq.(3) with approximation.

The kinetic curves for normal distribution starting at the origin and obtained for selected of B=4;5;6;7;8;9. are shown in Fig.3 and Fig.4. Analogous for the case of Rosin-Rammler–Sperling distribution were obtained for modified Eq.(3) if $n \in <0.04;105>$. The obtained results are shown in Fig.5. and Fig.6. The description of a kinetics in terms of Eq.(3) in terms of Eq.(3) with a condition:

$$B = \frac{\overline{R}}{2\delta^2} \ge 4 \tag{18}$$

means that for $\overline{R}=1$ the mean deviation cannot exceed 0.3535 ($\delta \le 0.3535$).

Hence a mathematical description of the process under consideration in terms of Eq.(3) becomes possible if the value of R remains within the limits $0.5R \le R \le 1.5R$ i.e. if the variability range of R is relatively small.

In the case of polydisperse solid material with Rosin - Rammler–Sperling distribution the nature of the distribution depends on the value of n. , the distribuants and density functions accept different forms for each individual value of n as in Fig.7 and Fig.8.



Fig.7. Distribuants and density function for Eq.(3)normal distribution.



Fig.8. Distribuants and density function for Eq.(3)-Rosin-Rammler-Sperling distribution.

The same procedure is applied for Eq.(2) and (4).

4 Conclusion

The results of numerical calculations for those equations are as follows:

Eq. F1.(2), F0.(3) and D1.(4) describe the process of thermal dissociation of polydisperse solid materials with normal grain size distribution for the values of B=3;4;5;6-Eq.(2) and B=4;5;6-Eq.(3) and B=0.78-Eq.(4).

For polydisperse materials characterized by Rosin -Rammler–Sperling distribution the description is possible only for a very small values of

 $n \in \langle 0.03; 0.09 \rangle$.Eq.(2) and $n \in \langle 0.04; 0.05 \rangle$ for Eq.(3) but for $n \in \langle 0.5; 0.55 \rangle$ in terms of Eq.(4).

A summary of hitherto consideration has been presented in tables 1 and 2 in which kinetic equations have been given for both types of grain size distribution and variability ranges are given for the limits, in which the initial equations provide a good description of the obtained curves or at least of some fragments of the curves. One may assume, therefore, that thermal dissociation of polydisperse solid materials can not be properly described in terms of kinetic equations in a general case, unless the grain size distribution has been taken into account.

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Description	Eq. type	Final Eq.	
of equation		For normal distribution	
F1	$-\ln(1-\alpha) = kt$	$\bar{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta}^{\theta} e^{-\theta/\theta} \cdot \exp\left[\Theta - I\right]^2 \right] d\theta \right\}$	
F0	α=kt	$\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_{1}}^{\theta} e^{-\theta/\theta} \cdot \exp\left[\Theta - \Omega\right]^{2} d\theta \right\}$	
D1	$\alpha^2 = kt$	$\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{q}^{0} \left(1 - \sqrt{Q} \right) d\theta \right\} = \left\{ \sqrt{\frac{B}{\pi}} \int_{q}^{0} \left(1 - \sqrt{Q} \right) d\theta \right\}$	
F0 D1	$\alpha = kt$ $\alpha^2 = kt$	$\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_{i}}^{\theta} e^{-\theta/\theta} \cdot \exp\left[\Theta(\theta - 1)^{2}\right] \right\}$ $\overline{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_{i}}^{\theta} (1 - \sqrt{\theta}/\theta) \cdot \exp\left[\Theta(\theta - 1)^{2}\right] \right\}$	

Table.1. The juxtaposition of of obtained Kinetic Equations describing the mean value of transformation degree $\overline{\alpha}$ for initial Eqs.(2),(3) and (4) for normal distribution.

Description of equation	Range of B	Variation limits of o For B
F1	B <i>∈</i> <3;7>	0.006-0.93
F0	B <i>∈</i> <5;11>	0.013-0.99
D1	B <i>∈</i> <0.78;0.85>	0.039-0.47

Table.2. The range of B values and the variation limits of α for B for Eqs.(2),(3) and (4) for normal distribution.

Description	Eq. type	Final Eq.
of equation		For normal distribution
F1	$-\ln(1-\alpha) = kt$	$\overline{\alpha} = 1 - \left\{ n \int_{\theta_{1}}^{\theta} e^{-\theta_{1}/\theta} \cdot \theta^{t-1} \cdot \exp[-\theta^{t}] d\theta \right\}$
F0	α=kt	$\overline{\alpha} = 1 - \left\{ n \int_{\theta_{l}}^{\theta} e^{-\theta_{l}/\theta} \cdot \theta^{l-1} \cdot \exp[-\theta^{l}] d\theta \right\}$
D1	$\alpha^2 = kt$	$\bar{\alpha} = 1 - \left\{ n \int_{q}^{\theta} \left(1 - \sqrt{\theta} / \theta \right) \cdot \theta^{-1} \cdot \exp[\theta d\theta] d\theta \right\}$

Table.3. The juxtaposition of of obtained Kinetic Equations describing the mean value of transformation degree $\overline{\alpha}$ for initial Eqs.(2),(3) and (4) for Rosin-Rammler-Sperling distribution.

Description of equation	Range of n	Variation limits of o For n
F1	n <i>∈</i> <0.03;0.09>	0.006-0.93
F0	n <i>∈</i> <0.04;0.05>	0.067-0.99
D1	n <i>∈</i> <0.50;0.55>	0.003-0.92

Table.4. The range of n values and the variation limits of α for n for Eqs.(2), (3) and (4) for normal distribution.

Experimental verification was performed in case of studying the kinetics of thermal dissociation for polydisperse systems -naturally occurring calcite and predicated calcium carbonate with normal and Rosin – Rammler - Sperling distributions and to determine the possibility of using the kinetic equations for the description of experimental data obtained for some model reaction.

The experimental results (kinetic curves) were compared with the theoretically derived curves and the usability of the selected kinetic models for description of the kinetics in such systems was estimated.

The model materials used in the experimental work were: manually ground natural calcite characterized by a normal grain size distribution and precipitated calcium carbonate characterized by the Rosin-Rammler-Sperling distribution and at the end conclusion are as follows:

- The knowledge of the dimensionless values of B, n, R_z and θ enables the determination of the maximum time of conversion for individual fractions, and a direct of the kinetic parameters of the process of thermal dissociation in polydisperse systems both in the case of normal and Rosin-Rammler-Sterling distributions.
- Conformity between the experimental curves and the calculated ones for Eq. F0 (3) and Eq. D1 (4) enabled to state that the new kinetic equations may be used for description of the process of thermal dissociation in ploydisperse systems after the grain size distribution has been determined Fig.10 and Fig.11.

- Determination of the nature and the type of the grain size distribution enables a proper selection of the kinetic equation and a description of the process of thermal dissociation of solids in polydisperse system.



Fig.10.Theoretical kinetic curves with experimental curves for Eq.(3) for calcite – normal distribution – temperature : 700° C.



Fig.11.Theoretical kinetic curves with experimental curves for Eq.(4) for calcium carbonate – Rosin-Rammler-Sperling distribution – temperature : 720° C.

References:

- J.Pysiak, Thermal Analysis of solids, International Journal of Thermal Analysis, 9, 49, 1995.
- [2] J.Pysiak, Roczniki Chemii, *Polish .J. Chem*, 44, 2229, 1970.
- [3] J.Pysiak, B.Pacewska and E. Arciszewska, Rocniki Chemii, *IPolish .J. Chem.*, 49, 645, 1795, pp. XX-XX.
- [4] J.Deren, J.Haber and R.Pampuch, *Chemistry of Solid State (in Polish)*, PWN, Warsaw, 1975.
- [5] M. E.Brown, Handbook of Thermal Analysis and Chemistry, Vol.1, Elsevier, Amsterdam, 1998.
- [6] S. Bretsznajder, Problems of Designing the Processes of Chemical Industry, (in Polish), Warsaw,1956.
- [7] M. Maciejewski, Thermal Dissociation of Solids (in Polish), Warsaw University, 1988.
- [8] A. Malecki and B. Malecka, Statistical methods for processing of the results of measurements, Shoo of Thermal Analysis, Zakopane, Poland,2002.